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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

AUG 16 1995

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: **Methyl Bromide.** Magnitude of the Residue in Processed Commodities: Instant White Rice, Shelled Roasted Peanuts, Unpopped Corn, and Country Ham.
CBRS No.: 15511
DP Barcode No.: D215044
MRID No.: 43629701
Chemical No.: 053201
Reregistration Case No.: 0335

Bonnie Cropp-Kohlligian

FROM: Bonnie Cropp-Kohlligian, Environmental Scientist
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Chemistry Branch II: Reregistration Support
Health Effects Division [7509C]

THRU: Robert Quick, Acting Section Head
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TO: Larry Schnaubelt/Barry O'Keefe [PM-72]
Reregistration Branch
Special Review and Reregistration Division [7508W]

Attached is a review of methyl bromide magnitude of the residue data (MRID 43629701) depicting residues of methyl bromide in/on instant white rice, shelled roasted peanuts, unpopped corn, and country ham resulting from postharvest fumigation with methyl bromide. This review was completed by Dynamac Corporation under the supervision of CBRS/HED. This review has undergone secondary review in the branch and has been revised to reflect Agency policies.

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The submitted methyl bromide residue data for instant white rice, shelled roasted peanuts, unpopped corn, and country ham (MRID 443629701) are deemed adequate. These data, together with previously submitted methyl bromide residue data for flour, corn meal, rolled oats, dry cake mix, parmesan cheese, and dried eggs (MRID 43025201; reviewed by R. Perfetti, 5/6/94), indicate that a food additive tolerance for residues of methyl bromide in/on processed foods, excluding chocolate, should be established at 10 ppm.

Since the subject methyl bromide residue data are adequately representative of processed foods and depict residues of methyl bromide in/on food matrices representing a wide range of possible oil content, these data are also deemed adequate to depict residues of methyl bromide in/on processed feed commodities resulting from postharvest fumigation with methyl bromide. Therefore, a feed additive tolerance for residues of methyl bromide in/on processed feeds should be established at 10 ppm.

If you need additional input please advise.

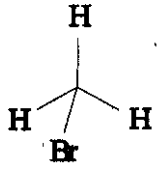
Attachment 1: Registrant's Response to Residue Chemistry Data Requirements.

cc: BLCKohlligian (CBRS), RBPerfetti (CBRS), MeBr Reg. Std. File, MeBr SF, RF, Circulate, and Dynamac.

RDI: RQuick: 8/10/95 RPerfetti:8/11/95 EZager:8/15/95

7509C:CBRS:BLCKohlligian:CM#2:Rm 805B:703-305-7462:8/9/95.

METHYL BROMIDE



Shaughnessy No. 053201; Case 0335

(CBRS Nos. 15511, DP Barcode D215044)

REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

BACKGROUND

The Methyl Bromide Reregistration Standard Update (6/91) required data depicting residues of methyl bromide in processed foods that are fumigated during storage. The Methyl Bromide Industry Panel (MBIP) submitted magnitude of the residue data for processed foods that were reviewed by the Agency (CBRS Nos. 12896, 12946, 12948, 12951, 12952, 12953, and 12955 and DP Barcode Nos. D197515, D197516, D197517, D197518, D197519, D197520, and D197228, R. Perfetti, 5/6/94). The Agency concluded that before an appropriate tolerance for processed foods could be determined, data were required depicting residues of methyl bromide in/on milled rice, popcorn, peanuts, and meats following methyl bromide fumigation. In response, the Grocery Manufacturers of America submitted data (1995; MRID 43629701) depicting residues of methyl bromide in/on instant white rice, shelled roasted peanuts, unpopped corn, and country hams following postharvest fumigation with methyl bromide. These data are reviewed here to determine their adequacy in fulfilling residue chemistry data requirements. The Conclusions and Recommendations in this document pertain only to the magnitude of the residue in processed food commodities.

The qualitative nature of the residue in plants is adequately understood; the residue of concern is methyl bromide *per se* (R. Perfetti, CBRS No. 8601, 9/24/91). Tolerances for residues of methyl bromide in/on food and feed commodities are currently expressed in terms of inorganic bromide [40 CFR §180.123, §180.199 and §185.3480]. However, the Agency has determined that inorganic bromide is not of toxicological concern and is requiring the registrant to propose tolerances for methyl bromide to replace the inorganic bromide tolerances. As there are no Codex MRLs for residues of methyl bromide, there are no questions with respect to Codex/U.S. tolerance compatibility.

An adequate method is available for enforcement of the current tolerances for inorganic bromide and is listed in PAM, Vol. II as Method I. For determining residues of methyl bromide *per se*, a GC/ECD headspace assay method [King et al., *J. Agric. Food Chem.*, 29(5), 1003-1005, 1981] is available for data collection and tolerance enforcement. This method has been forwarded to the FDA for inclusion in PAM, Vol. II as Method A.

CONCLUSIONS/RECOMMENDATIONS

The submitted residue data for instant white rice, shelled roasted peanuts, unpopped corn, and country ham are adequate. The current submission, together with previously reviewed residue data for processed foods (R. Perfetti, 5/6/94), indicate that a food additive tolerance for residues of methyl bromide in/on processed foods, excluding chocolate, should be established at 10 ppm.

Since the subject methyl bromide residue data are adequately representative of processed foods and depict residues of methyl bromide in/on food matrices representing a wide range of possible oil content, these data are also deemed adequate to depict residues of methyl bromide in/on processed feed commodities resulting from postharvest fumigation with methyl bromide. Therefore, a feed additive tolerance for residues of methyl bromide in/on processed feeds should be established at 10 ppm.

DETAILED CONSIDERATIONS

Residue Analytical Methods

In conjunction with the methyl bromide magnitude of the residue study, the registrant submitted method descriptions (1995; MRID 43629701) for the analysis of methyl bromide residues in/on instant rice, shelled roasted peanuts, unpopped corn, and country ham. Residues of methyl bromide were determined using the modified King GC/ECD headspace method #93-001. This method was reviewed by the Agency (CB No. 3890, 7/14/88; and CBRS No. 4399, 11/3/88, C. Deyrup) and deemed adequate as an enforcement method for analysis of methyl bromide *per se* on plants.

Briefly, frozen samples are blended with water in a sealed container equipped with a sampling port. Residues are released by allowing the blended sample to equilibrate for 20 minutes at 25 $\pm$ 3 C. The headspace is sampled and residues are determined by GC/ECD. The residues are quantitated by comparison with a matrix standard curve, which is generated through the analysis of fortified control samples of each commodity on each day of analysis. The reported limit of quantitation (LOQ) for each commodity is 0.25 ppm. Chromatograms and sample calculations were provided. Analyses were performed by the Webb Technical Group, Inc., Raleigh, NC.

Concurrent recoveries from 8 to 11 control samples of each commodity fortified at ~0.4-3.7 ppm of methyl bromide ranged from 85.1-159% (Table 1). Four to five controls of each commodity bore nondetectable (<0.25 ppm) residues of methyl bromide.

The submitted analytical method is adequate for collecting data on residues of methyl bromide in/on instant rice, shelled roasted peanuts, unpopped corn, and country ham.

Table 1. Concurrent method recovery of methyl bromide from control samples fortified at ~0.4-3.7 ppm.

Commodity	Fortification level (ppm)	%Recovery	Number of samples [a]
Instant white rice	0.373-0.973	98.3-104	8
Peanuts	0.373-0.973	87.6-133	8 (1)
Popcorn	0.373-3.73	93.1-159	11 (3)
Country ham	0.373-3.73	85.1-158	11 (3)

[a] Number of fortified control samples with recoveries outside of the acceptable 70-120% range are listed parenthetically.

Storage Stability Data

The Agency (CB No. 6879, 7/30/90, N. Dodd) has concluded that residues of methyl bromide in/on raw agricultural commodities are stable when samples are stored on dry ice for up to 12 hours, and that storage stability data are necessary only for samples stored in excess of 12 hours.

All samples in the current submission were stored at -10 C for $\leq$8 hours until analysis. No additional storage stability data are required.

Magnitude of the Residue in Plants and Processed Food Commodities

In response to the Methyl Bromide Reregistration Standard Update (6/91), the Methyl Bromide Industry Panel (MBIP) submitted magnitude of the residue data for processed foods (R. Perfetti, 5/6/94). The data submitted for flour, corn meal, rolled oats, dry cake mix, parmesan cheese, and dried eggs were deemed adequate. Processed food commodities were fumigated for 24 hours at 3 lb ai/1000 ft^3, forced-air ventilated to allow the methyl bromide concentration to reduce to <5 ppm, and aerated in-chamber for 24 hours. Maximum residues of methyl bromide in/on samples collected 24 hours following the fumigation, ventilation, and aeration ranged from <0.25 ppm in/on parmesan cheese to 8.25 ppm in/on flour. The Agency concluded that based on the available data, a food additive tolerance needs to be established for processed foods, excluding chocolate products, which would be covered under a separate tolerance. However, before an appropriate food additive tolerance for processed foods could be determined, data were required depicting residues of methyl bromide in/on milled rice, popcorn, peanuts, and meats sampled 24 hours after one 24-hour fumigation at 3 lb ai/1000 ft^3 at a minimum temperature of 10 C and an in-chamber aeration period of 24 hours.

Two methyl bromide end-use products (100% PrGs, EPA Reg. Nos. 5785-11 and -41) are currently registered for fumigation of processed foods. The registrant has been required to revise all labels pertinent to processed foods to reflect the use pattern supported by the residue data (R. Perfetti, 5/6/94). The 1x application rate is considered to be the rate

supported by the previously submitted residue data (24-hour fumigation at 3 lb ai/1000 ft^3 and an in-chamber aeration of 24 hours).

The Grocery Manufacturers of America submitted data (1995; MRID 43629701) depicting residues of methyl bromide in/on instant white rice, shelled roasted peanuts, unpopped corn, and country hams following a single application of methyl bromide at ~3 lb ai/1000 ft^3. Commodities were fumigated in typical commercial packaging materials. Commodities in duplicate chambers occupied ~32% of the chamber volume. Chamber temperatures were held at 10±3 C throughout the study. Samples were fumigated for 24 hours. The chambers were then opened and forced-air ventilated for ~24 minutes to allow the methyl bromide concentrations to reduce to ≤5 ppm. The chambers were subsequently closed for an additional 24-hour in-chamber aeration prior to taking the 0-hour samples. Chamber doors were opened only to allow for sampling and recording the temperature. Samples of rice and peanuts were taken at 0-, 24-, 48-, and 96-hour sampling intervals. Samples of popcorn and country ham were taken at 0-, 24-, 48-, 96-, and 168-hour sampling intervals. For each commodity and chamber, duplicate samples were collected. All samples were stored at -10 C for ≤8 hours until analysis. Four to five controls of each commodity bore nondetectable (<0.25 ppm) residues of methyl bromide.

Residues of methyl bromide were determined using the modified King headspace method (Method #93-001) described in the Residue Analytical Methods section of this report. Residues of methyl bromide in/on treated samples of each commodity are presented in Table 2. Maximum residues of methyl bromide in/on samples collected at the 24-hour sampling interval following one 24-hour fumigation and a 24-hour in-chamber aeration, ranged from <0.25 ppm in/on peanuts to 2.02 ppm in/on unpopped corn.

The submitted residue data for instant white rice, shelled roasted peanuts, unpopped corn, and country ham are adequate. The current submission, together with previously reviewed residue data for processed foods (R. Perfetti, 5/6/94) indicate that a food additive tolerance for residues of methyl bromide in/on processed foods, excluding chocolate, should be established at 10 ppm.

Table 2. Residues in processed food commodities following fumigation with methyl bromide at ~1x and in-chamber aeration.

Commodity	Application Data			Sampling Interval [a] (hours)	Methyl Bromide Residues (ppm) [b]
	Rate (lb ai/ 1000 ft^3)	Fumigation Interval (hrs)	Commodity Temp. (C)		
Instant white rice	3	24	10	0	0.592, 0.569 (0.432, 0.439)
				24	0.311, 0.297 (0.275, 0.281)
				48	<0.25, <0.25 (<0.25, <0.25)
				96	<0.25, <0.25 (<0.25, <0.25)
Shelled roasted peanuts	3	24	10	0	<0.25, <0.25 (0.307, <0.25)
				24	<0.25, <0.25 (<0.25, <0.25)
				48	<0.25, <0.25 (<0.25, <0.25)
				96	<0.25, <0.25 (<0.25, <0.25)
Unpopped popcorn	3	24	10	0	3.13, 3.00 (4.42, 4.38)
				24	1.58, 1.67 (2.02, 1.99)
				48	0.671, 0.709 (0.867, 0.891)
				96	0.292, 0.306 (0.291, 0.318)
				168	<0.25, <0.25 (<0.25, <0.25)
Country ham	3	24	10	0	2.62, 3.69 (3.46, 4.27)
				24	0.488, 0.667 (0.385, 0.852)
				48	0.438, 3.27, 0.118 (1.21, 0.550)
				96	0.577, 0.844 (1.06, 0.792)
				168	0.613, 0.449 (1.18, 0.975)

[a] The sampling interval represents the interval between completion of a 24 hour fumigation, a forced air ventilation of ~24 minutes to reduce methyl bromide concentrations to <5 ppm, and a 24 hour in-chamber aeration to sampling of the commodity.

[b] Two samples were taken from two duplicate chambers for each commodity. Residue values listed parenthetically are from the samples taken from the duplicate chamber.

MASTER RECORD IDENTIFICATION NUMBERS

The citation for the MRID document used in this review is presented below.

43629701 (1995) J. Ussary, R. Moseman, and S. Tracey. Fumigation of Processed Foods with Methyl Bromide: Magnitude of the Residues. Laboratory Project Identification P8. Unpublished study prepared by Webb Technical Group, Inc. 145 p.

AGENCY MEMORANDA CITED IN THIS DOCUMENT

CBRS Nos: 12896, 12946, 12948, 12951, 12952, 12953, and 12955
Subject: Response to the Methyl Bromide Reregistration Standard: Residue Data.
From: R. Perfetti
To: L. Rossi
Date: 5/6/94
MRID(s): 43025801, 43025701, 43029801, 43025101, 43025202, 43023601, and 43025301

CBRS No.: 8601
Subject: Methyl Bromide Industry Panel: Response to the Methyl Bromide Reregistration Standard: Metabolism Study.
From: R. Perfetti
To: W. Burnam and L. Rossi
Date: 9/24/91
MRID(s): None.

CB No.: 6879
Subject: Methyl Bromide Reregistration Letter and Attachments from the Methyl Bromide Industry Panel Dated 5/25/90.
From: N. Dodd
To: W. Francis
Date: 7/30/90
MRID(s): None.

CB No.: 4399
Subject: Follow-up to Methyl Bromide Registration Standard. Methyl Bromide Industry Panel Response (9/22/88) to DEB Review of 7/14/88 on Postharvest Protocol, Analytical Methodology, and Storage Stability.
From: C. Deyrup
To: J. Kempter
Date: 11/3/88
MRID(s): None.

CBRS No: 3890
Subject: Follow-up to Methyl Bromide Registration Standard. Post Harvest Protocol, Interim Plant Metabolism Report, Analytical Methods, and Storage Stability.
From: C. Deyrup
To: J. Kempter
Date: 7/14/88
MRID(s): 40579501, 40607801, and 40618501.